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Non-equilibrium fast thermal response of polymers

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ABSTRACT

Non-equilibrium thermal response of polymers at nanosecond and longer time scales is described by linear differential equations with dynamic heat capacity in the framework of the linear response theory. The equation can be utilized on the length scale of more than 10 nm for semi-crystalline polymers and down to the nanometer scale for amorphous system. Self-consistent analytical solution for non-equilibrium thermal response of polymers under pulse heating in planar and spherical geometries is obtained. Non-equilibrium thermal response of polymers under pulse heating differs significantly from the thermal response of materials in equilibrium. It is noteworthy that even very fast components of the dynamic heat capacity (with relaxation time in the order of 1 ns) significantly affect the thermal response to the local thermal perturbations (at nanometer scale). This can be significant for the heat transfer process at fast formation of crystallites on nanometer scale.

1. Introduction

Recent advances in thin-film ultra-fast calorimetry showed the possibility to generate non-equilibrium states and to study phase-transition kinetics at microsecond and even faster time scales [1–29]. Phase transitions and nucleation mechanisms in metals were investigated by ultra-fast calorimetry [11]. Controllable quenching based on the ultra-fast scanning nanocalorimetry was applied to investigate the nucleation and crystallization kinetics in technologically important polymers [12–25]. Ultra-fast scanning calorimetry was applied to study superheating [1–29],22,26] and to prevent fast reorganization in polymers during melting and crystallization [27]. The technique can be applied towards micro- and even nanoscale objects to study kinetics of thermodynamic processes at fast cooling and heating rates up to 10^7 K/s [1–29],10,29]. Furthermore, the method provides the possibility of temperature-modulation experiments at frequencies up to the megahertz range [28].

Increasing of the rate of the temperature change in the calorimetric experiments requires a comprehensive analysis of the non-equilibrium thermal response of polymers and polymer-based composites at fast temperature change and high frequency temperature modulation. The short-time thermal phenomena are important for the thermal design and processing of micro- or nano-systems [30–32]. Contemporary trends in nanoscale devices and manufacturing promotes rapidly growing interest in non-equilibrium fast thermal response of technologically promising materials [33,34]. The classical heat transfer theory can be insufficient for ultra-fast processes in nanoscale systems. The effect of non-Fourier heat conduction can be considerable, when the sample parameters are sharply varying in space and time [35–41]. Then, the limits of validity of classical heat conduction theory to polymers and polymer composites under fast and local thermal perturbations should be determined.

Besides, relaxation processes related to dynamic heat capacity of polymers are significant in a wide range of thermal perturbations [42–46]. The spectrum of relaxation time of thermal excitations in polymers is wide-ranging, as follows from the experiments on broadband dielectric spectroscopy and heat capacity spectroscopy [42–58]. The molecular dynamics in polymers is quite complex and involves short- and long-scale motions, especially in the amorphous phase [59–62]. This can cause a broadband dispersion of the thermal properties. Time-dispersion of the heat capacity in polymers and organic liquids have been intensively investigated [42,45,58,59,63–68]. Similarly, the thermal conductivity can reveal the time-dispersive behavior as follows from the linear response theory [69]. There is discussion in literature regarding the time-dispersion of the thermal conductivity [38–41,70,71]. The question “how significant the effects of the time-dispersion for the thermal conductivity of polymers?" requires an answer. The low frequency experiments prove non-dispersive behavior of the thermal conductivity simultaneously with the broadband dispersion of the heat capacity [66]. Nevertheless, the question on the dispersion of the thermal conductivity in polymers at high frequencies still has no clear answer. Thus, the heat transfer in polymers under fast thermal

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